

Frenkel-Kontorova Model of Vacancy-Line Interactions on Ga/Si(112)

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We develop an exactly solvable microscopic model for analyzing the strain-mediated interaction of vacancy lines in a pseudomorphic adsorbate system. The model is applied to Ga/Si(112) by extracting values for the microscopic parameters from total-energy calculations. The results, which are in good agreement with experimental observations, reveal an unexpectedly complex interplay between compressive and tensile strain within the mixed Ga-Si surface layer.

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When a material is grown pseudomorphically on a lattice-mismatched substrate, the resulting strain field can lead to self-organized structures with a length scale many times the atomic spacing. One well known example is the Ge/Si(001) dimerized overlayer system. The Ge film is compressively strained (by 4% relative to the bulk), and the system lowers its energy by creating dimer vacancies in the surface layer; at the vacancy sites, the exposed atoms in the second layer rebond to eliminate their dangling bonds. The missing-dimer vacancies order into vacancy lines (VLs) with $2 \times N$ periodicity, where the optimal N depends on the Ge coverage [1]. Even for coverages as low as a few monolayers, the concept of elastic strain relaxation within a coherent pseudomorphic Ge film is appropriate. For example, Tersoff showed theoretically for a three-layer Ge film that the equilibrium N corresponds to the vacancy density at which the compressive stress from the Ge overlayer cancels the tensile stress from the rebonded missing dimers [2].

For monolayer and lower coverages, the concept of strain relaxation becomes problematic, because the strain within a partial overlayer becomes difficult to define. In this Letter we develop a model for analyzing such situations and apply it to another VL system, Ga on Si(112). We show that despite striking similarities in the phenomenology, the underlying energetics of Ga/Si(112) is rather distinct from Ge/Si(001). To make our treatment physically transparent but also quantitatively accurate, we develop an exactly solvable model of VL interactions in which the microscopic parameters are extracted directly from first-principles total-energy calculations. This model contains only nearest-neighbor harmonic interactions but reproduces the first-principles results quite accurately, and thus allows for a particularly simple analysis of the dominant interactions.

When Ga is deposited on Si(112) and annealed, a well-ordered surface is formed consisting of large (112)-oriented domains, as shown in Fig. 1. The VLs are oriented horizontally in Fig. 1. Even at room temperature, the VLs show minimal thermal meandering—only

single kinks (up or down by one lattice spacing) are observed in scanning tunneling microscopy (STM). The mean VL spacing in Fig. 1 is 5.2, with the distribution sharply peaked around 5 and 6. The microscopic structure of VLs on Ga/Si(112) is shown in Fig. 2. Since Ga is trivalent it prefers to adsorb at threefold surface sites. The bulk-terminated Si(112) substrate, which may be regarded as a sequence of double-width (111)-like terraces and single (111)-like steps, offers just such threefold sites at the step edges, as shown in Fig. 2(b). A single Ga vacancy leaves two step-edge Si atoms exposed, which rebond to form a dimer. This model was first proposed by Jung *et al.* [3] and subsequently confirmed by Baski *et al.* [4] using STM and total-energy calculations. It predicts that two adjacent Ga vacancies will be very unlikely—because the three Si atoms exposed can form

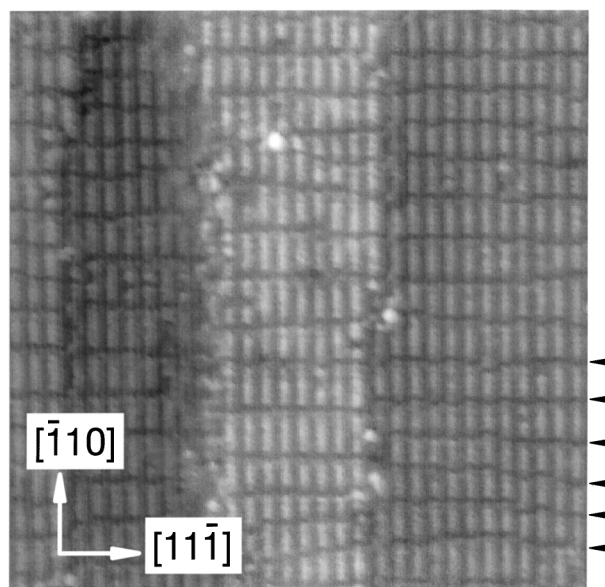


FIG. 1. Empty-state STM image ($300 \times 300 \text{ \AA}$) of Ga/Si(112). The wedges mark the vacancy lines, which are oriented along the $[11\bar{1}]$ direction (and are interrupted by a narrow monolayer-high terrace in the center of the figure).

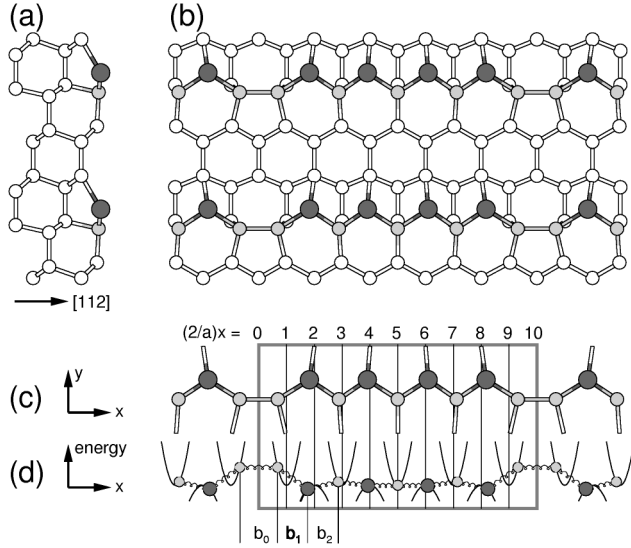


FIG. 2. (a) Side and (b) top views of Ga/Si(112) with vacancy period $N = 5$. The fully relaxed coordinates are from first-principles total-energy minimization. (c) Bonding chain of Ga (dark) and Si (light) atoms. (d) One-dimensional Frenkel-Kontorova model representing this Ga-Si chain. The (horizontal) atomic displacements, u_j , are defined relative to the ideal positions (shown by thin grid lines) of the substrate atoms; vertical displacements represent the individual substrate-strain energies, $(1/2)k_j u_j^2$, appearing in Eq. (1).

only one dimer, resulting in an extra Si dangling bond; indeed, there are no adjacent vacancies visible in Fig. 1. In this way, VLs on Ga/Si(112) are essentially constrained to have a fixed width of one vacancy.

To construct a microscopic model for the interactions between VLs we make three simplifying assumptions about their ground-state structure. (1) We take the VLs to be perfectly straight; this turns a two-dimensional surface problem into an effective one-dimensional system. (2) We assume this one-dimensional system to be periodic with a single vacancy per unit cell; that is, the vacancy separation is taken to be $L = Na$, where N is an integer and a is the surface lattice constant. (3) Full structural relaxation within the local-density approximation, described below, shows that the Si substrate atoms are essentially unperturbed from their ideal locations (Fig. 2 shows the relaxed geometry for $N = 5$; substrate atoms are white). Thus, we consider the vacancy-vacancy interaction to be mediated entirely by the bonding chain of Si and Ga atoms shown in Fig. 2(c).

We now map this Ga-Si chain (with vacancy period N) onto a one-dimensional chain of harmonic springs connecting N Si atoms and $N - 1$ Ga atoms in a unit cell of length Na , as shown in Fig. 2(d). The bonding of each atom, j , to the substrate is also taken to be harmonic, with potential minima at the ideal substrate positions. This is a variant of the Frenkel-Kontorova (FK) model, which has been widely used to study complex static and dynamical phenomena arising from purely local interactions. Within

the FK model, the total (potential) energy is

$$U = \sum_{i=0}^{2N-2} \frac{1}{2} K_i (b_i - b_i^{\text{eq}})^2 + \sum_{j=1}^{2N-1} \frac{1}{2} k_j u_j^2. \quad (1)$$

Here the one-dimensional atomic displacements u_j are defined with respect to the ideal positions of the substrate atoms, $(a/2)j$, and the corresponding spring lengths b_i are defined in Fig. 2(d). This FK model has six parameters: within each unit cell, one spring represents the Si-Si bond at the vacancy (with spring constant K_{Si} and equilibrium length $b_{\text{Si}}^{\text{eq}}$), while the remaining $2N - 2$ springs represent the Ga-Si bonds (with spring constant K and equilibrium length b^{eq}). Two different substrate spring constants, k_{Si} and k_{Ga} , represent the bonds from Si and Ga atoms in the chain to the rigid substrate.

To solve for the displacement field that minimizes the FK energy, we first consider the force equations for atoms away from the vacancies, and then apply the boundary conditions due to the vacancies. In equilibrium, the force on atom j is given by

$$F_j = 0 = K(2u_j - u_{j-1} - u_{j+1}) + k_j u_j, \quad (2)$$

which can be written for the Si or Ga sublattice as

$$[(2K + k_{\text{Ga}})(2K + k_{\text{Si}}) - 2k^2]u_j = K^2(u_{j+2} + u_{j-2}). \quad (3)$$

In the continuum limit (large N) this becomes a simple differential equation,

$$[\beta - 1]u(x) = (a/2)^2 u''(x), \quad (4)$$

where we have defined

$$\beta = \left(1 + \frac{k_{\text{Si}}}{2K}\right) \left(1 + \frac{k_{\text{Ga}}}{2K}\right). \quad (5)$$

Equation (4) shows that the continuum displacement field, $u(x)$, has an exponential solution with the decay length $(a/2)/\sqrt{\beta - 1}$. Note that for the case of weak binding to the substrate, $k_j \ll K$, this decay length reduces simply to $\sqrt{K/k} (a/2)$, where k is the average substrate potential.

For the discrete case (arbitrary N), Eq. (3) provides a recurrence relation whose solutions have the form

$$u_j = c_1^{\text{Si,Ga}} e^{2\lambda j} + c_2^{\text{Si,Ga}} e^{-2\lambda j}, \quad (6)$$

where $e^{\pm 2\lambda}$ are given by

$$e^{\pm 2\lambda} = \sqrt{\beta} \pm \sqrt{\beta - 1}. \quad (7)$$

The general form of the discrete solutions is again seen to be exponential, although with a somewhat more complicated form for the (dimensionless) decay length, $(2\lambda)^{-1}$. It is easy to verify by Taylor expansion that for weak substrate binding we again recover the correct limiting behavior, $(2\lambda)^{-1} \rightarrow \sqrt{K/k}$.

Equation (2) provides the following relationship between the four coefficients c_n^{Si} and c_n^{Ga} , which are used for the Si and Ga sites, respectively:

$$\frac{c_n^{\text{Ga}}}{c_n^{\text{Si}}} = \sqrt{\frac{1 + k_{\text{Si}}/2K}{1 + k_{\text{Ga}}/2K}}. \quad (8)$$

It is convenient to introduce a dimensionless parameter, Λ , defined by equating the right-hand side of Eq. (8) with $\exp(2\Lambda)$. The deviation of Λ from zero measures the relative difference in strength between Si- and Ga-substrate binding, and will give rise (see below) to oscillations in the strain field around the simple exponential behavior found in the continuum limit.

The remaining unknowns are determined by the boundary conditions at the vacancies. By applying these we arrive at the exact closed-form solution for the displacement field and corresponding bond lengths. For example, the Si-Si vacancy-bond length, as a function of the vacancy period, can be written as

$$b_0(N) = a - \frac{2u_1^\infty}{1 + \xi \{ \coth[2(N-1)\lambda] - 1 \}}, \quad (9)$$

where u_1^∞ and ξ (both positive) are combinations of the various FK parameters [5]. The Ga-Si bond lengths have a more complicated form due to the two different substrate potentials,

$$b_i(N) = \frac{a}{2} + 4c \{ \cosh\Lambda \sinh\lambda \cosh[(2i - 2N + 1)\lambda] \pm \sinh\Lambda \cosh\lambda \sinh[(2i - 2N + 1)\lambda] \}, \quad (10)$$

where the last term (present only when $\Lambda \neq 0$) is positive and negative for even- and odd-numbered bonds, respectively. The magnitude of the strain field is given by the prefactor $c = (1/2)(b_0 - a)e^{-\Lambda} \text{csch}[2(1 - N)\lambda]$. It is evident from Eqs. (9) and (10) that the strain field is characterized by a single length scale, $(2\lambda)^{-1}$, which describes both the relaxation of each bond with respect to the distance, i , from a vacancy, and the relaxation of all strains with respect to the vacancy period, N .

To apply this general solution to Ga/Si(112) we must determine numerical values for the six FK parameters (two bond lengths, b^{eq} and $b_{\text{Si}}^{\text{eq}}$, and four spring constants, K , K_{Si} , k_{Ga} , k_{Si}) appearing in Eq. (1). We do this either analytically from the Stillinger-Weber potential (for Si-Si parameters) or numerically from first-principles total-energy calculations (for Ga-Si parameters). These calculations were performed in a double-sided slab geometry with six layers of Si and a vacuum region equivalent to five layers of Si. Total energies and forces were calculated within the local-density approximation (LDA) with gradient corrections [6], using Troullier-Martins pseudopotentials and a plane-wave basis with a kinetic-energy cutoff of 8 Ry, as implemented in the FHI96MD code [7]. Total energies were completely converged with respect to Brillouin-zone

sampling. Full structural relaxation was performed on all atoms except those in the innermost double layer until the surface energies were converged to 0.1 meV/Å².

Using the equilibrium structure of Ga/Si(112) with no vacancies we find that, for small displacements, $k_{\text{Si}} = 2.0 \text{ eV/Å}^2$ and $k_{\text{Ga}} = -0.7 \text{ eV/Å}^2$. The negative spring constant here indicates that in the absence of defects the Ga sublattice is at a point of unstable equilibrium—a finding confirmed by our LDA results for finite N (below). From calculations on isolated infinite Ga-Si chains, we obtain $K = 9.8 \text{ eV/Å}^2$ and $b^{\text{eq}} = 2.00 \text{ Å}$. This equilibrium bond length implies a 4% compressive epitaxial strain with respect to the Si substrate, and contributes to the driving force for vacancy formation in Ga/Si(112). Finally, by expanding the radial part of the Stillinger-Weber potential about the LDA vacancy bond length for $N = 2$, we obtain $K_{\text{Si}} = 5.5 \text{ eV/Å}^2$ and $b_{\text{Si}}^{\text{eq}} = 2.25 \text{ Å}$.

We now compare the structural predictions of the FK model to those of first-principles calculations. Using the LDA approach described above, supercells with vacancy periodicities from $N = 2$ to 8 were completely relaxed. Figure 3 shows the FK and LDA results for the vacancy-bond length vs N and for the Ga-Si chain bond lengths for $N = 8$. The agreement is remarkably good, especially considering the simplicity of the model. Note the oscillatory behavior of the Ga-Si FK bond lengths—due to the unequal Ga- and Si-substrate binding strengths—which is strikingly confirmed by the LDA results.

We turn next to the description of strain energetics and, thereby, the effective VL interaction. Within the FK model, we use Eqs. (9) and (10) to evaluate the strain energy, U , for arbitrary N . By exploiting the fact that the sums over atomic sites are geometric series, we obtain a

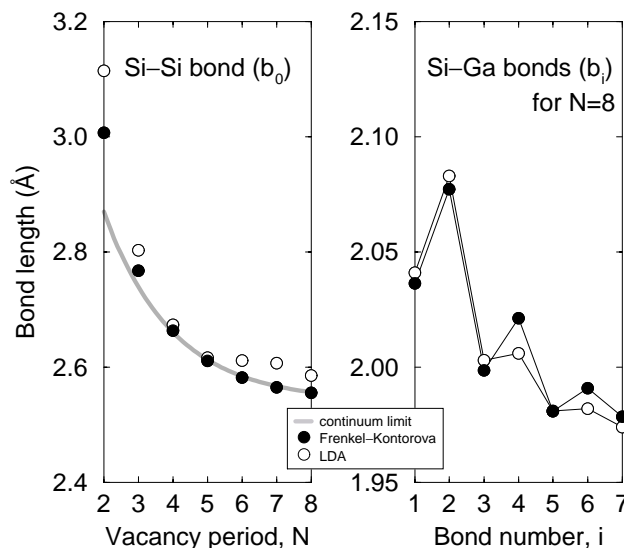


FIG. 3. Equilibrium bond lengths from the FK model and LDA. Left: Si-Si vacancy-bond length vs vacancy period. Right: Ga-Si bond length vs “bond number” [relative distance from the vacancy bond, as defined in Fig. 2(d)].

closed-form solution for $U(N)$ [5]. It is important to note that energies for different N are not directly comparable, since the number of Ga atoms per unit length varies with N . In general, this is resolved by considering the surface free energy (per unit area),

$$\gamma(N) = (NA)^{-1}[E_t(N) - (N - 1)\mu_{\text{Ga}}]/2, \quad (11)$$

where $E_t(N)$ is the (LDA) total energy for a Ga/Si(112) cell with vacancy period N , and μ_{Ga} is the Ga chemical potential (the energy per atom of bulk Ga). The chemical potential is not derivable within the FK model, but must be included “by hand.” We do this by defining $\gamma^{\text{FK}}(N)$ analogously to Eq. (11), with a fictitious chemical potential adjusted to give identical VL formation energies, ε_f , within the FK model and LDA (which gives $\varepsilon_f = -43 \text{ meV}/\text{\AA}$).

In Fig. 4 we show the resulting FK and LDA surface energies, relative to the limit of large N . The LDA energy minimum occurs at $N = 6$, in excellent agreement with the experimental results for this system, while the FK minimum is only slightly higher, at $N = 8$. The energy scale for the effective VL interaction is extremely small: relative to infinite separation between vacancies, the LDA energy minimum is only of order $2 \text{ meV}/\text{\AA}^2$, while the FK result is about half this value. In general, the agreement between the two results is quite remarkable, considering the length scale of the vacancy spacing, the smallness of the energy scale, and the extreme simplicity of the FK model.

By analyzing the individual contributions to the FK strain energy, it is now simple to identify the dominant physical mechanism determining the equilibrium VL spacing. In Fig. 4 we plot (as small dots) only those terms in Eq. (1) representing strains within the Ga-Si bonding chain, and exclude the contribution from the Si-Si rebonded dimer as well as all interactions between the

chain and substrate atoms. *It is clear that this Ga-Si chain strain completely dominates the energetics for all physically relevant densities.* This result has two important implications. (1) The role of the rebonded Si dimers, although obviously crucial for eliminating the dangling bonds created by the Ga vacancies, plays no further significant energetic role in determining the equilibrium VL spacing in Ga/Si(112). This is quite different from the role of the rebonded Ge-dimer vacancies in Ge/Si(001), for which the tensile stress contribution has been shown to cancel the compressive contribution from the overlayer only at the proper density [2]. (2) While a low density of Ga vacancies allows for relief of compressive strain, when their density becomes too high, part of the Si-Ga bonding chain experiences *tensile* strain—which acts as a repulsive interaction between VLs. This effect is readily visible in the right panel of Fig. 3. Relative to the equilibrium Si-Ga bond length of 2.00 \AA , bonds far from the vacancy (numbered 5–7) are compressively strained, bonds near the vacancy (3–4) are essentially unstrained, but bonds very close to the vacancy (1–2) are tensilely strained. This tensile contribution begins to dominate the surface energy at about $N < 5$.

In summary, we have developed a Frenkel-Kontorova model to analyze the microscopic origins of vacancy-line interactions on Ga/Si(112). The model reveals that the mechanism of strain relaxation in this submonolayer adsorbate system is quite complex. In particular, we have identified the microscopic origins of attractive and repulsive interactions between vacancy lines: both are mediated by a combination of compressive and tensile bond strains within a single chain of Ga and Si atoms. The sum of these strain energies is minimized at a vacancy-line density very close to the experimentally observed value. In general, we expect the future analysis of similar strain-induced self-organized adsorbate systems to benefit from this type of simple but accurate analytical model.

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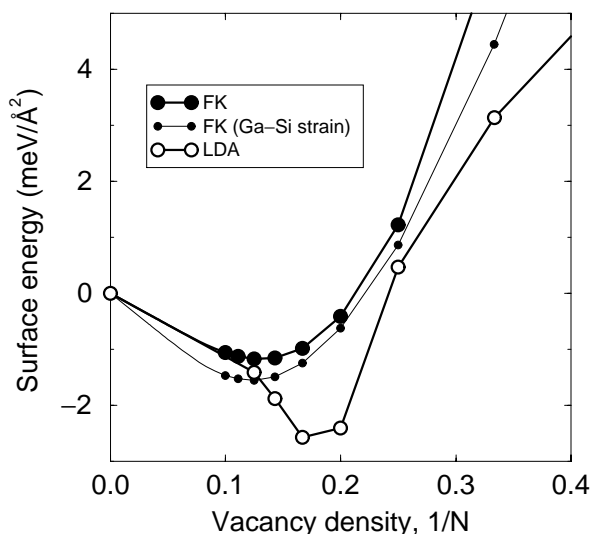


FIG. 4. Relative surface energies, $\gamma(N)$, vs vacancy density, calculated within the FK model and LDA.

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